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Adsorption study of acrylamide-tertiary-butyl sulfonate (ATBS)/ acrylamide copolymer in polymer flooding enhanced oil recovery (EOR) process

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Abstract. Polymer flood is known as the most important enhanced oil recovery technology due to its various advantageous and relatively cheaper price. However, it comes with associated problems of polymer adsorption that leads to injectivity loss. This work aims in studying various parameters that may affect the ATBS/ Acrylamide copolymer adsorption in a porous medium to optimize the polymer scheme. Synthetic D brine with D sand sample was mixed and tested in static and dynamic condition. These tests were conducted at room temperature and 90°C whereby the core flooding experiments were conducted with varied flowrate through Berea Sand Core sample. Results show that a higher brine salinity and a longer aging time leads to higher adsorption rate whereas adsorption static test conducted at replicated reservoir condition of 90°C resulted in lower adsorption capacity than at room temperature. Also, static adsorption was found to be higher than the dynamic adsorption due to the changes in the specific surface area and the extent of mechanical retention present in the dynamic core flood experiment. In conclusion, the type of polymer used in polymer flooding must be carefully chosen to serve the need for a specific reservoir condition so that the adsorption phenomenon is minimized.

1. Introduction

Polymer flooding appears to be one of the most attractive and promising EOR techniques owing to the abundant resources of polymer plus relatively cheaper price compared with other surfactants. In the polymer flooding method, water-soluble polymers increase the viscosity leading to a more efficient displacement of moderately viscous oils [1,2]. This polymer will be retained in the porous medium to cause some reduction of the rock permeability, which can contribute to the oil recovery mechanism. In this work, ATBS containing polyacrylamides copolymer (see Figure 1(a)) with proprietary additives that show the best resistance to radical and thermal degradation of up to 110°C was chosen as the tested polymer considering the field parameter such as temperature and salinity [3]. Posthydrolyzed polyacrylamides are composed of a wide range of anionic chains, and this acrylamides sodium acrylate copolymer results in a polymer with a more even charge distribution along the backbone that is vital for the behaviour of the polymers in an aqueous solution, especially in the presence of divalent cations while the neighboring effect offered by ATBS provides tolerance to divalent containing brines and protection



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to hydrolysis for higher temperature [1,3,4].

However, excessive polymer retention resulted in a loss to rock by adsorption, entrapment, salt reactions will eventually cause loss of injectivity and causing a delay in polymer propagation through porous media [5-8]. It is postulated that there may be significant interactions between the transported polymer molecules and the porous medium where such interactions caused the polymer to be unnecessarily retained in the porous medium. This may lead to the formation of a bank of injection fluid wholly or partially denuded of the polymer. Clearly, this bank of fluid will have a viscosity which is much lower than the injected polymer solution, and this will generally reduce the efficiency of the polymer flood [9].

Generally, the retention of polymer tends to reduce oil recovery despite the permeability reduction contribution in aiding the oil recovery. In fact, the level of polymer retention is one of the key factors in determining the economic viability of a polymer flood. There are three main retention mechanisms which are thought to act when polymer solutions flow through porous media which are polymer adsorption; mechanical entrapment; and hydrodynamic retention as suggested by [9] in Figure 1(b).

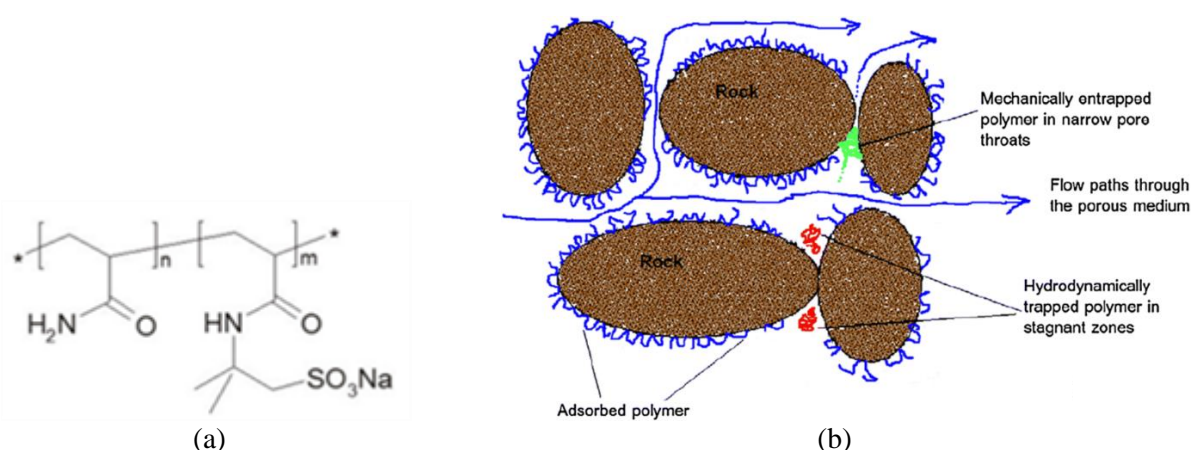


Figure 1. (a) Example of acrylamide- ATBS copolymer [4] and (b) Polymer retention mechanism in porous media [9].

Polymer adsorption may be defined as the interaction between the polymer molecules and the solid surface-as facilitated by the solvent which caused the polymer molecules to be bound to the surface of the solid i.e. polymer occupies surface adsorption sites; mainly by physical adsorption - Van der Waal's and hydrogen bonding; rather than by chemisorption, in which full chemical bonds are formed between the molecule and the surface [9]. Basically, it was observed that a higher levels of adsorption achieved when a larger surface area available. Evidently, researchers observed there are further complications within a consolidated (or unconsolidated) porous medium in that there may be regions of the solid surface that cannot be accessed by the polymer where these molecules generally are adsorbed onto the rock surface by the mean of an overall low free energy [10-12].

Retention by mechanical entrapment is occurring when larger polymer molecules become lodged in narrow flow channels [5,6] as shown in Figure 1b) along with the other retention mechanisms. This mechanism has been studied by several authors [5,6,13-15]. As the polymer solution passed through this complex network, the molecules would take various routes and some molecules would be trapped in the narrow pores. These would block, and flows in these elements would consequently reduce, probably trapping more molecules upstream of the blockage. This mechanism is very similar to the well-known phenomenon of deep-bed filtration [16].

Hydrodynamic retention of polymer is the least well defined and understood retention mechanism. These were concluded from experimental observation in which after steady state was reached in a polymer retention experiment in a core, the total level of retention changed when the fluid flow rate was adjusted to a new value [5,6,17-19].

In this project, the adsorption phenomena resulting in loss of polymer quantity during the enhanced oil recovery process is studied. Several factors that may affect this adsorption phenomena such as brine concentration, temperature, the type of lithology of the rock formation, aging time in static and dynamic condition was further investigated in this project. From this investigation, the problem of loss of polymer during the EOR process can be minimized leading to a more efficient displacement.

Static adsorption has been determined by using the final concentration of each sample. The final concentration was read from the linear equation generated from the standard curve (generated from UV-Vis analysis) of each reading. Polymer adsorption was determined using the following equation:

$$\text{Polymer adsorption, mg/g} = \frac{\text{Vol.of polymer (initial polymer conc - final polymer conc)}}{\text{Weight of rock (g)}} \quad (1)$$

Dynamic adsorption has also been determined by using the final concentration of each sample read from the linear equation that resulted from the standard curve of each reading.

$$\begin{aligned} \text{Polymer adsorbed (mg)} &= \text{Theoretical amount of polymer (mg)} - \text{Actual amount of polymer (mg)} \\ \text{Theoretical amount of polymer (mg)} &= \text{Volume polymer injected (L)} \times \text{Initial concentration (mg/L)} \\ \text{Actual amount of polymer (mg)} &= \text{Volume polymer collected (L)} \times \text{Core measured polymer (mg/L)} \\ \text{Polymer adsorption (mg/g)} &= \text{polymer adsorbed (mg)} / \text{weight of rock (g)} \end{aligned}$$

Researchers claimed that for a polymer-retention value more than 200 $\mu\text{g/g}$, polymer retention can have a serious impact on the oil-displacement rate and the economics of polymer flooding [8].

2. Methodology

This work aims in studying various parameters that may affect the ATBS/ Acrylamide copolymer adsorption in porous medium including temperature, brine salinity, aging time and the lithology of a sand sample in the effort of optimizing the polymer scheme. Synthetic D brine of various salinity with D sand sample which taken at various depth was mixed and tested in static and dynamic (core flooding) condition. Two liters of D synthetic brine containing 35000 ppm and 30000 ppm of NaCl respectively have been prepared with the composition of original D injection water is shown in Table 1. AN 125 SH polymer (Co-polymers of ATBS and acrylamide) has been prepared by adding 1g of polymer into 199g of water by using a mixer as per the polymer solution preparation. For the static adsorption, the large surface area of the sand was being in static condition with the polymer. These tests were conducted at room temperature and 90°C where the mixed rock/ solution samples were analyzed using UV-Visible so that the adsorption rate can be determined (Figure 2).

Dynamic adsorption was studied whereby the polymer solution will move throughout the core in the core flooding equipment with a varied flow rate of 0.5 ml/min and 0.15 ml/m through Berea Sand Core sample. The dimensional of the core itself needs to be measured (1" x 6") and the pressure and the temperature of the core flood unit were set to replicate the reservoir condition (temperature of 25°C and 90°C, confining pressure of 2000 psi and back pressure regulator of 50 psi). Effluent from the core holder was collected to measure the adsorption by using the UV-visible equipment (Refer Figure 3).

Table 1. The D injection water composition.

Chemical	CaCl ₂	MgCl ₂	SrCl ₂	Na ₂ SO ₄	NaCl	KCl	NaHCO ₃
Weight (g/2L)	2.4130	20.3634	0.0258	33.0864	7.6916	1.2378	0.4490

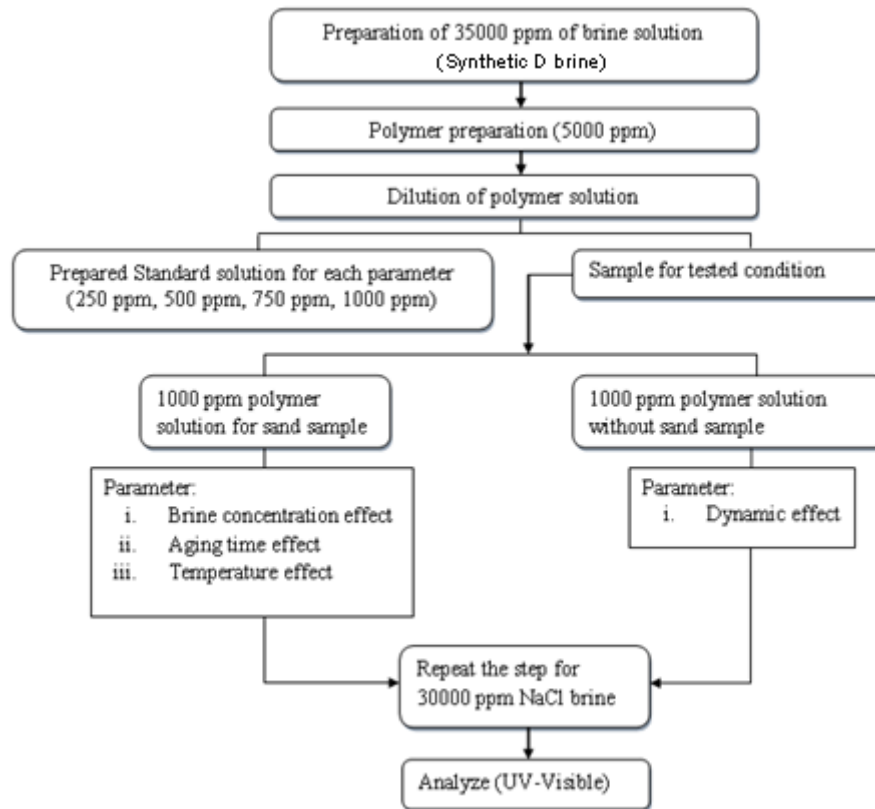


Figure 2. Static and dynamic adsorption test.

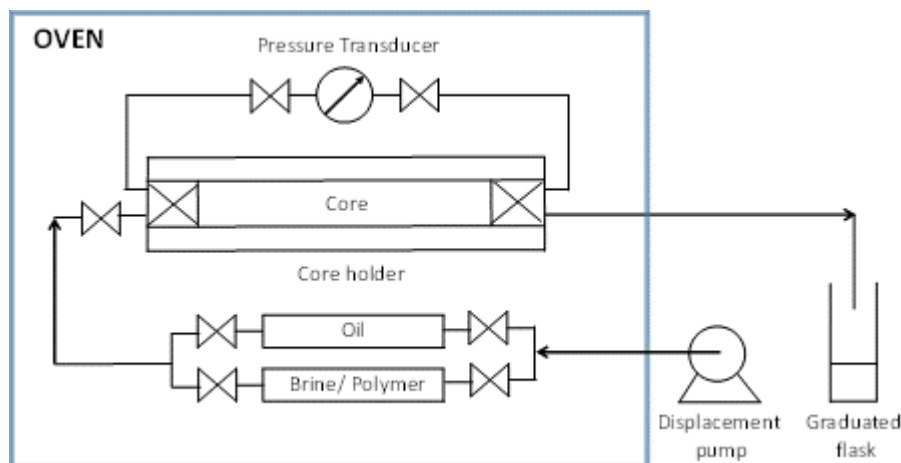


Figure 3. Dynamic adsorption study in core flooding experiment.

3. Result and Discussion

3.1 Effect of different brine salinity on the polymer adsorption

Based on results shown in Figure 4, polymer adsorption increases with increase in salinity which is in agreement with [20]. This may be due to the attraction between a different charge of the polymer and the rock surface which resulted in higher ionic strength between the solutions with the rock surface for higher salinity. Since the rock surface also contains the cationic substances, the engagement between the different ionic will be higher than the 30000 NaCl ppm injection water. The rock surface possesses the negative surface charge and will attract the positive charge from the solutions sample. According to

[20], as the salt concentration increases, charge shielding takes place due to positively charged ions of the salt (Na^+); thus the hydrodynamic radius of polymer molecule reduces. Due to this intermolecular interaction, electrostatic repulsion in the polymer solution decreases resulted in an increased in adsorption capacity of polymer solution.

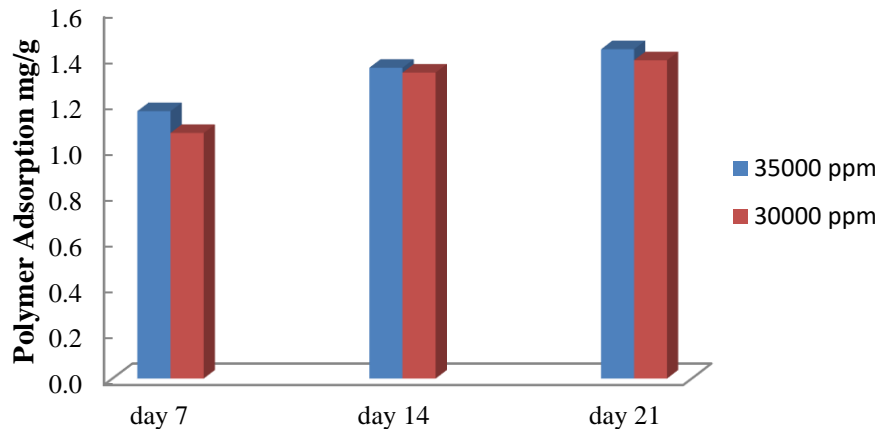


Figure 4. Effect of different brine concentration on polymer adsorption.

3.2 Effect of the aging time on the polymer adsorption

The polymer solution was tested at the static condition in the various sand sample with 35000 ppm and 30000 ppm brine respectively for 7, 14 and 21 days of aging time (Figure 5). It was clearly observed that higher adsorption of the polymer solution was achieved with the increasing of aging time. This is because of more contact time of polymer solution with the rock surface. This behavior is also expected by polymer hydrolysis as explained by [21,22]. They found that the viscosity was increased with increasing aging time and this may be explained by acrylamide moieties that hydrolyzed to negatively charged acrylate, increasing the intra-chain charge repulsion, thus causing an increase in viscosity hence higher adsorption was observed.

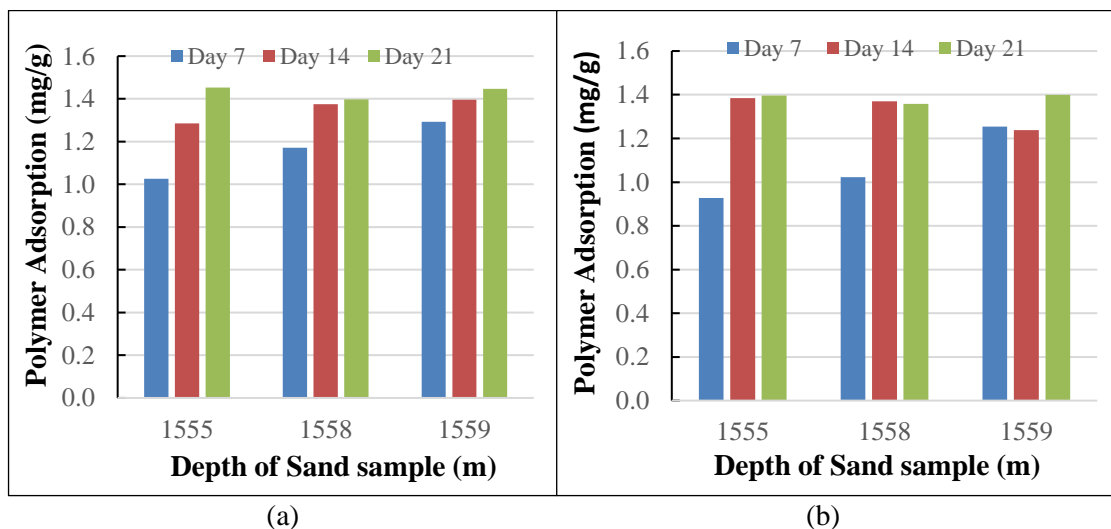


Figure 5. Effect of the aging time on polymer adsorption in (a) 35 000 ppm and (b) 30 000 ppm NaCl concentration.

3.3 Effect of the different sand sample on the polymer adsorption

The sand sample used in this test was acquired at the depth of 1555 m, 1558 m and 1559 m from D well. The lithology investigation of the sand sample revealed all sand sample having relatively almost the same mineralogy composition of all depth; the amount of carbonates around 2.21 wt%, total clays about 14.35 wt%, feldspar about 2.45 wt% and quartz around 81 wt% and no pyrite and halite stated on the core sample. Hence, the effect of the different depth of sand samples did not give too much impact on adsorption activities. It is worth note that the effect of pressure and also the temperature for every depth of sand sample were not taken into considerations in these experiments but the results shown were entirely based on the mineralogy condition. Research by [23] revealed a small amount of clay (predominately negative charge of the clay mineral) can cause a significant increase in polymer retention. It was observed experimentally that in general, the deeper the acquired sand sample, the higher retention rate for all parameters being studied, though this worth further investigation (Figure 6). This may due to the deeper sand sample have a higher specific surface area that resulted in higher adsorption as explained by [24]. Hence, it is worth to further study this effect by varying the amount of clay and specific surface area.

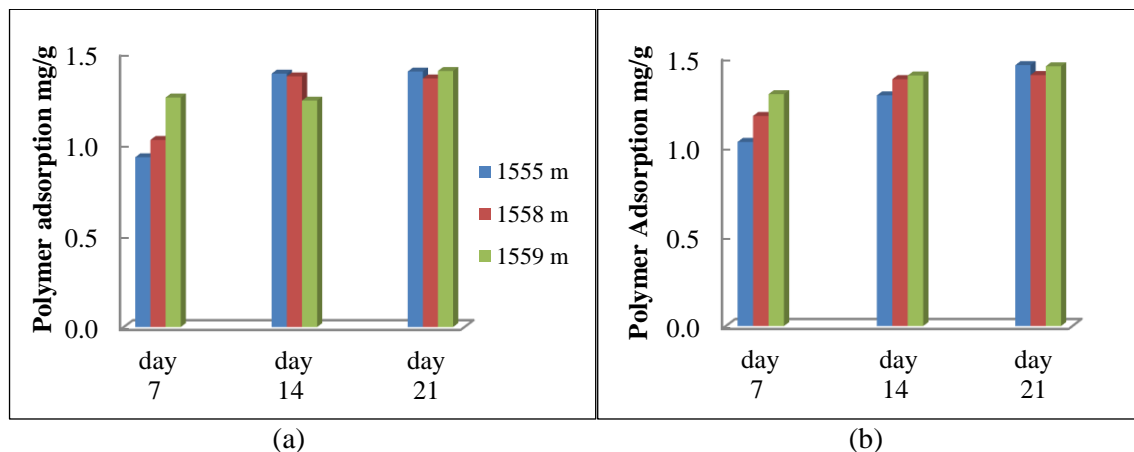


Figure 6. Effect the sand sample mineralogy on polymer adsorption in (a) 35 000 ppm and (b) 30 000 ppm NaCl concentration.

3.4 Effect of temperature on the polymer adsorption

The polymer solution was further tested at different temperatures of room temperature and 90°C to replicate the actual D reservoir temperature. It can be seen from Figure 7 that, lower adsorption was achieved in the high temperature (i.e. reservoir temperature of 90°C) than the room temperature. According to [25] and [26], the high temperature causes the polymer structure to degrade and the bond of the structure may break leading to the polymer become lighter and it may flow to the porous media smoothly; hence the polymer is less adsorbed. The mothers chained in the polymer were broke causing the ionic strength between the chained also become weaker. Thus, less adsorption or attraction occurred due to the less ionic strength engagement. This may be explained by the combination of electrostatic forces and molecular forces (like hydrogen bond, Van der Waals, hydrophobicity, etc.) causes both anionic (ATBS) and non-ionic (acrylamide) polymers adsorption to decrease with temperature. The high-temperature increased negative charge on the rock surface hence high repulsion (with anionic monomers-ATBS) occurs which lowers adsorption. In addition to that, non-ionic polymers (acrylamide) adsorption is related to hydrogen bond, therefore, an increase in temperature can easily break the bond causing adsorption to decrease [27].

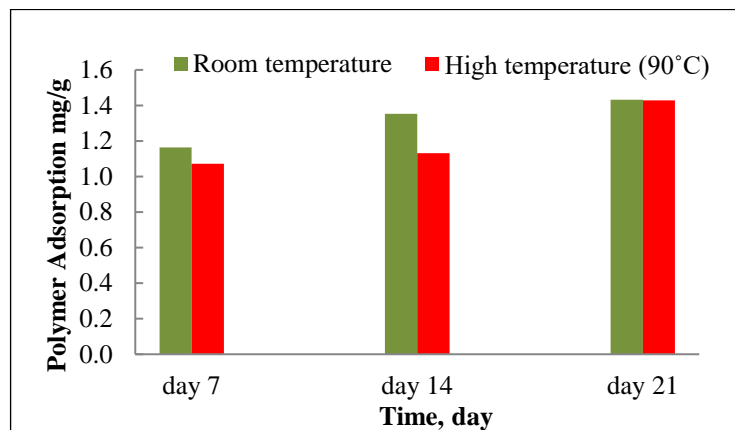


Figure 7. Effect of reservoir's temperature on polymer adsorption.

3.5 Polymer adsorption in dynamic condition

A different flow rate of 0.15 ml/min and 0.5 ml/min has been studied for the dynamic adsorption test. Based on the result shown in Figure 8, a lower flow rate will give the higher adsorption. This is because the low flow rate giving more contact time for the polymer passing through the porous media, hence giving more opportunity for the polymer to stick and retain onto the porous medium. However, dynamic adsorption/ retention in a porous medium is a complex process to study than static adsorption since the polymer may be retained in the pore structure by other means, for example in dead-end pores or in pore throats.

By comparing the adsorption for both static and dynamic condition, it is obvious that the static adsorption is far higher than the dynamic adsorption by the factor of more than 1000 times. Again, this may be explained by the time contact between the polymer solution and the rock surface. Longer contact time was experienced by the polymer solution with the rock samples in the static adsorption than in the dynamic condition through the core sample. The static test allowed higher retention time as the rock/polymer was in static (no motion) which eventually resulted in higher adsorption. In addition to that, the actual reservoir crushed core was used in the static test which means higher surface area per unit volume for polymer adsorption to take place. Dynamic adsorption/ retention in a porous medium is far more complex than the static adsorption since the polymer may be retained in the pore structure e.g. in dead-end pores or in pore throats; in addition to adsorption onto the surface of the rock. The presence of inaccessible pore volume (IAPV) accelerates the polymer through the porous rock because the large ATBS molecules cannot penetrate into all pore space that is available [25].

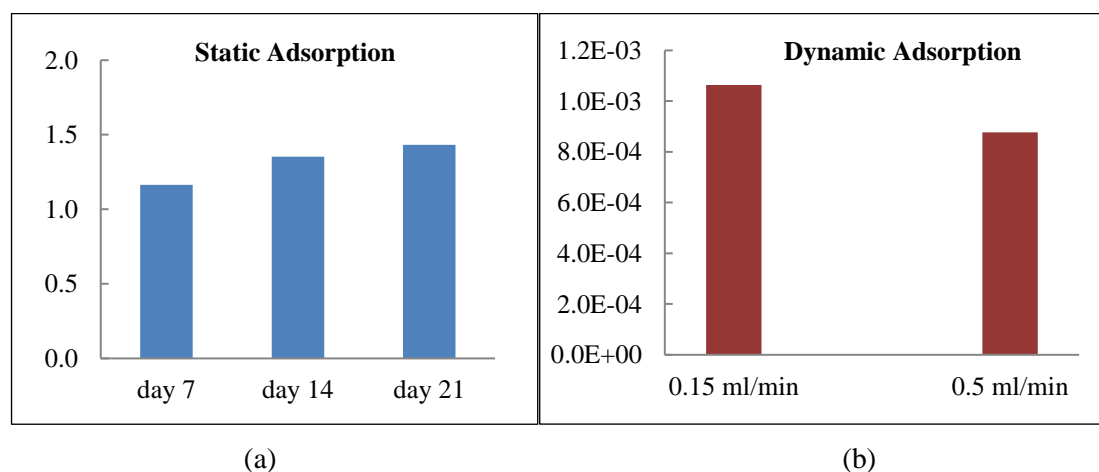


Figure 8. Effect of the (a) static and (b) dynamic adsorption in 35 000 ppm NaCl concentration.

4. Conclusions

It has been shown that all parameters studied in this work have an effect on the adsorption phenomena. Higher salinity, longer aging time, lower temperature have led to higher adsorption rate. Different mineralogy may also affect the polymer adsorption due to different charge attractions may occur and cause the adsorption. However, the effect of the sand sample in this study is minor because the entire sand sample was taken at the relatively same depth of 1555 to 1559 m in which lithology analysis revealed they are having almost the same mineralogy. The factors influencing polymer adsorption, mechanical entrapment, and hydrodynamic retention were identified and studied in this work. In summary, the flow of polymer solutions through porous media is a complex phenomenon which requires a detailed understanding of retention, flow capacity alteration, as well as inaccessible pore volume. Hence, an estimation of these parameters is crucial for economic evaluation and slug design for a successful implementation of polymer flooding EOR.

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